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Effect of synthetic modifiers on the rheology of coating colours

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The effect of synthetic modifiers on the coating colour rheology was studied. Also the influence of the pigment system was studied. Six different polymers were studied in two pigment systems. In the solely ground calcium carbonate (GCC)-containing formulation polymers were studied with three different addition levels. GCC/clay-based formulation was tested with one polymer addition level in order to study rheology; water retention, Brookfield viscosity and Hercules high shear were measured.

Study showed that increase in high shear decreased water retention. The effect on rheology was the greater the more modifier was added to the coating colour. There were differences among hydrophobic alkali-swellable emulsion (HASE) type thickeners. Clay-containing coating colour had larger thickening effect. HASE type modifier increases low shear viscosity, and decreases high shear. Influence on dewatering rate is moderate. Alkali-swellable emulsion (ASE) thickener improved water retention, and left the high shear value on lower level than HASE. The surface of the plays a significant role in the thickening effect of the modifier.

Keywords	coating, thickener, rheology, water retention, HASE

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Insinöörityön tarkoituksena oli tutkia paperin ja kartongin päällystyksessä käytettyjen synteettisten lisäaineiden vaikutusta pastan reologiaan. Työssä tutkittiin myös, miten pigmenttisysteemi vaikuttaa synteettisten paksuntajien tehoon. Kokeellisessa osuudessa vertailtiin kuutta eri lisäainetta, joista viisi oli paksuntajia ja yksi sideaine. Paksuntajat olivat tyyppejä HASE (hydrophobic alkali-swellable emulsion) ja ASE (alkali-swellable emulsion).Pigmentteinä jauhettuja karbonaatteja sisältäneessä reseptissä lisäaineita tutkittiin kolmella eri annostasolla. Karbonaatti/kaoliini pigmenttisysteemissä lisäaineiden toimintaa arvoitiin yhden annostason avulla. Vaikutuksia reologiaan tutkittiin mittaamalla vesiretentio, matalan leikkausnopeuden Brookfield-viskositeetti ja korkean leikkausnopeuden Hercules-viskositeetti.

Yleisesti ottaen vesirention parantuessa korkean leikkausnopeuden viskostiteetti nousee. Muutos on sitä suurempi, mitä enemmän lisäainetta on käytetty. Lisäaineiden välillä oli toiminnallisia eroja. HASE nostaa viskositeettia matalilla leikkausvoimilla ja laskee korkean leikkausnopeuden viskositeettia. ASE paksuntajalla korkean leikkausnopeuden viskositeetti jäi matalammalle tasolle kuin HASE:lla. Kaoliinia sisältävä pasta paksuuntui suhteessa enemmän, koska pigmenttien pinnan muodot vaikuttavat merkittävästi polymeerin kiinnittymisen. Sillä oli myös merkittävästi parempi vesiretentio.

Avainsanat	Paperin päällystys, paksuntaja, reologia, vesiretentio, HASE

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I wish to thank my supervisor Mika Kosonen for excellent teaching, and my instructor Mikko Mäkinen for the relentless support and never ending faith in me. Furthermore, I wish to thank Anneli Lepo and Helena Peuranen for their guidance. A very special thanks goes to my children Riku and Linnea. Thank you for being so understanding towards mom’s cranky days. And finally, my dearest husband, Jouni. I could not have done this without your support and love. Thank you for taking care of our home and the kids, thank you for loving me and letting me fulfil my dreams.

Contents

List of abbreviations

ÅA-GWR	Åbo Akademi gravimetric water retention analyzer
ACT	Associative cellulosic thickener
ASE	Alkali-swellable emulsion
ATH	Alumina trihydrate
$CaCO_3$	Calcium arbonate
CMC	Carboxymethyl cellulose
GCC	Ground calcium carbonate
HASE	Hydrophobic alkali-swellable emulsion
HEUR	Hydrophobic ethoxylated urethanes
LWC	Lightweight coated paper
OBA	Optical brightening agent
PCC	Precipitated calcium carbonate
PEG	Polyethylene glycol
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
SA	Styrene-acrylate
SB	Styrene-butadiene
SC	Solids content
STDA	Short time dwell application
WR	Water retention

List of symbols

G'	storage modulus
G''	loss modulus
η	viscosity
τ	shear stress
$\dot{\gamma}$	shear rate

1 Introduction

Most paper grades are coated with aqua based coatings to change the substrate's surface properties because many of these paper grades are printed later in the cycle. Coating affects substrates printing properties through opacity, smoothness, porosity, strength, and various other physical properties. Coating colour rheology plays very important role in a successful coating procedure. Coating colours used in the coating process are subjected to various rheological phenomena. Undesired rheological behaviour can easily affect negatively the coating machine runnability, thus weakening the product's quality, and in the worst case, producing brakes at the coating station. The latter means lost time and money. These rheological phenomena can be controlled with rheological modifiers, called thickeners.

This thesis was made for Kemira Plc., Fiber and wet end department. Kemira is a global multifunctional company, paper segment presenting itself as the core business. The purpose of the thesis was to study synthetic thickeners, their mechanism and effect of different dosing levels in coating colour formulations. The theoretical part and the evaluation of results are based on two different kind of coating colour formulations, where different types of thickeners are evaluated by their rheological performance.

2 Pigment coating

Coated products can be roughly classified into paper and board. End-use of these products determines desired quality. The main purpose of coating is to improve the surface quality of coated products. Coating changes the substrate's surface by filling the cavities and covering the surface of the base paper (Figure 1). One must remember that even though coating plays an important role in the end quality, 80 per cent of a coated paper's properties depend on the properties of base paper. Depending on the requirements, base paper can be coated from one to several layers of coating.
[1, s. 13.]

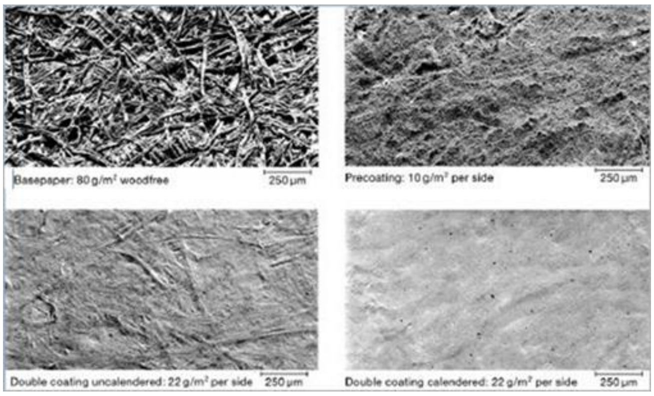

Figure 1. Uncoated and coated paper surfaces [2].

As earlier mentioned, in most cases papers are being printed. In this case, quality equals printability and visual appearance. Different printing methods set different requirements for the paper being printed. Most commonly printability requires controllable interaction between ink and the surface printed on. Coating increases brightness and smoothness, which results in better printed gloss. Opacity is increased due to high light scattering of pigments. Stiffness is improved as well as mechanical surface strength, which is a crucial property in a printing process. Applied coating layer reduces the penetration of ink into paper. This results sharper print image and possibly lower ink demand. Depending on the end use, board grades also require hydrophobic properties. All these needs are fulfilled by different coating formulations, right coating method, and finishing treatments. [1, pp. 12-13; 3, pp. 332-334.]

3 Coating methods

Coating is basically a procedure where coating colour is first applied on base paper, and then the excess colour is metered and dried. The difference between coating methods is in the way how coating colour is introduced to the web and how coating colour penetrates into the base paper. The penetration of coating colour in the base paper is dependent on the used method. With the penetration, the focus is on how water and binder penetrates the pores of the base paper. The amount of penetrating water is dependent on external pressure and the pressure penetration it causes. [4, pp. 191.]

3.1 Blade coating

Blade coating is the most common coating method, which is divided in three categories based on the choice of coating colour application. Selected method is dependent on the coat weight of the product and machine speed. The choices are:

- Roll application
- Short Dwell Time Application (SDTA)
- Jet application.

3.1.1 Applicator roll station

With the *roll application* (Figure 2), an excess of coating colour is applied on a paper web from a coating colour pan by an applicator roll. Then the colour thickness is adjusted with a metering element, usually a doctor blade, which can be either high or low angle (bend blade) blade. The time between the application and the metering is called dwell time. [5, pp. 472-473.]

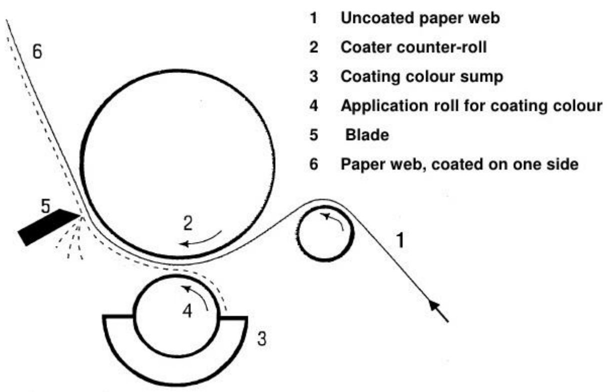

Figure 2. Principle of applicator roll coating station [6].
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The benefits of this method are the wide coat weight range, and the relatively good quality of the coated product [7, pp. 10].

3.1.2 SDTA coating station

SDTA is a coating station (Figure 3) where coating colour is fed into an application chamber through an opening in the chamber bottom. SDTA is really an application nozzle where a trailing edge of the nozzle is formed by the metering blade. The name short dwell refers to the very short time between coating colour and paper before the metering. [5, pp. 474-475.] Besides having a good runnability, STDA stations are easy and fast to clean [5, pp. 475].

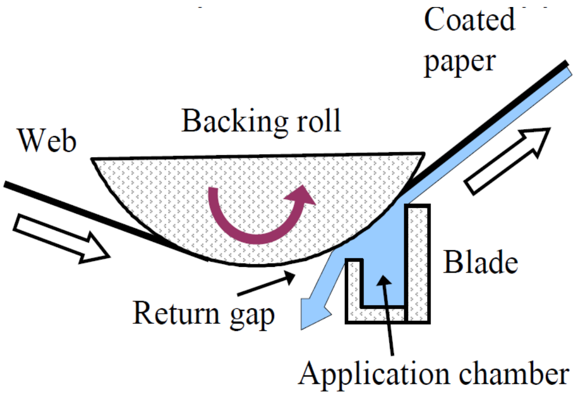


Figure 3. SDTA coating station [7, pp. 14].

3.1.3 Jet applicator coating station

A jet applicator is a nozzle, which sprays coating colour onto the web. Excess coating is scraped away by a metering blade, and then returned to the colour collection pan as shown in figure 4. [5, pp. 475-476.]

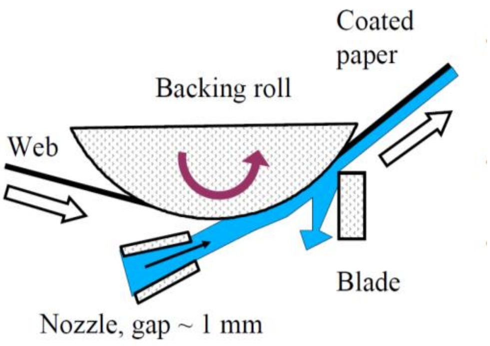


Figure 4. Principle of a jet applicator coating station [7, pp. 18].

The faster and sharper the coating spray feed is, the better jet application performs. The outcoming jet is laminar and therefore even. The amount of applied coating colour can be adjusted by changing the coating colour feed. The desired coat weight is achieved by adjusting the angle or pressure of the blade. Since the applied amount of coating colour is lower than that with an applicator roll, the blade pressures are lower and application is less sensitive for web brakes. [4, pp. 194; 7, pp. 19; 8.]

3.2 Curtain coating

Curtain coating is an application where the layer of colour falls by gravity onto the paper surface. The only metering device is the nozzle slice. The thickness of coating layer is achieved through the difference between the jet and running web speed. With curtain coating, the viscoelastic properties of the colour are very important since the falling colour layer has to be very uniform. [3, pp. 377-378.]

3.3 Film coating

Film coating is an example of indirect coating, where a coating film is created by a nip formed between two rolls. If chosen, both sides of the web can be coated simultaneously. Excess medium can be metered with either blade or rod. [3, pp. 376; 9, pp. 497.] Figure 5 illustrates the principal of film transfer coating.

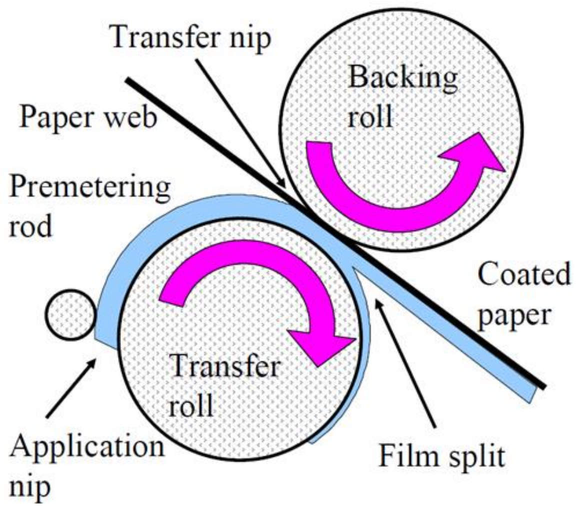


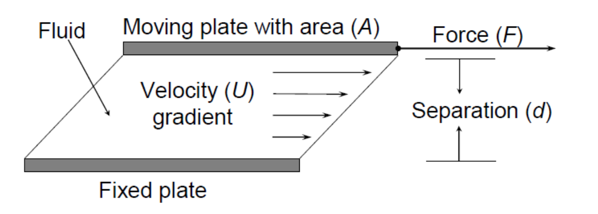
Figure 5. Illustration of the film transfer principal [12, pp. 6].

Among blade coating, film transfer is the most common coating method. Film transfer is ideal for high coating speeds and low coat weights. Viscosity plays an important role in the coating process; too low viscosity negatively affects coat weight development, whereas too high viscosity can enable undesired misting. [12, pp. 6-7].

4 Rheology

Rheology is a science that studies the flow of liquids and deformation behaviour of solids [10, pp. 13]. Liquids are divided into Newtonian, non-Newtonian, viscoid, and visco-elastic groups based on their rheological behaviour. Coating colours are seldom Newtonian, because their viscosity is rarely constant due to the presence of particles in coating colour. [4, pp. 184-185.] Coating colours are subjected to a wide range of shear stresses during the coating process, and the complex time-dependent rheological behaviour of colours can result structure breakdown under prolonged mixing. [11, pp. 318-319.]

For simplicity, the flow can be illustrated with the two plate model even though the real geometric conditions are not this simple in a rheometer measuring system [10, 16]. Figure 6 shows a fluid undergoing simple shear between plates.



Shear Stress	Shear Rate	Viscosity
τ = Force/Area / Nm^{-2} = Pa	$\dot{\gamma}$ = dU/dx / s^{-1}	$\eta = \tau / \dot{\gamma}$ / Pa.s (mPa.s)

Figure 6. Illustration of the two plates model and rheological terms [11, pp. 319].

The external force (F) is applied to the area (A) of the upper plate while the lower plate stays immovable. The resulting velocity (U) is measured and the shear rate is defined as the change in velocity between plates. The fluid between the plates resists the movement of the upper, plate and viscosity is defined as resistance to movement. [11, pp. 319.]

4.1 Flow behaviour

Fluids are divided into non-Newtonian and Newtonian groups. The latter one has constant viscosity in all shear rates and time. Viscosity of non-Newtonian fluid is dependent on shear rate [12, pp. 320] as shown in figure 7.

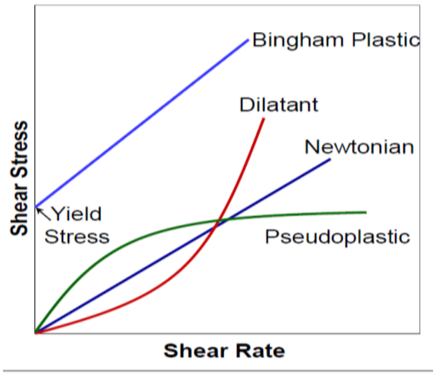


Figure 7. Shear rate versus shear stress [12].

There are two types of non-Newtonian fluids; shear thinning, often referred as pseudoplastic, and shear thickening (dilatant). Viscosity of pseudoplastic fluids decreases with increasing shear rate. Coating colours are known to be pseudoplastic fluids. Shear thickening behaviour is less common. [12, pp. 320]

4.2 Time-dependant rheology

When studying the coating colours, also time dependant rheology in under inspection. This is illustrated in Figure 8. Time-dependant flow is divided into rheopexy and thixotropy. [12, pp. 322.]

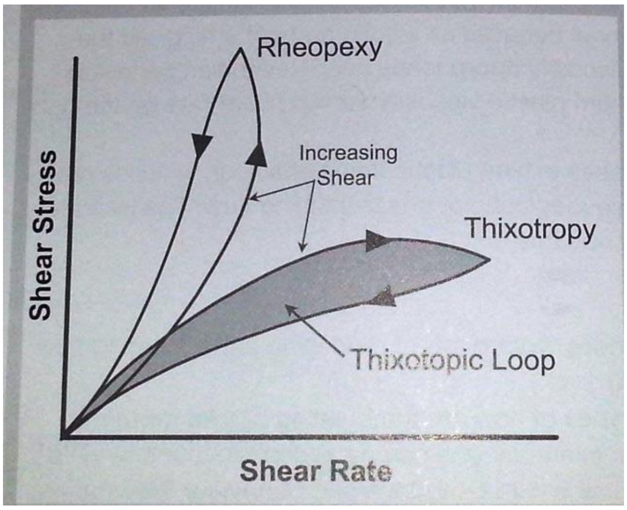


Figure 8. Types of time-dependant flow behaviour [12, pp.322].

The values are determined by calculating the difference between the downward curve and the shear stress axis. A negative value indicates rheopexy and a positive value thixotropy. The area between upward and downward curve is known as a hysteresis area, which expresses the loss of energy under strain. [10, pp. 67]

4.3 Viscoelastic behaviour

Viscoelastic behaviour refers to fluids which have both viscous and elastic solid-like properties. Paper coatings are considered viscoelastic. Viscoelasticity is often measured with oscillatory methods. Figure 9 illustrates a amplitude sweep curve. The storage modulus G' is considered elastic component and the loss modulus G'' viscous component. The vertical line in the rheogram represents the end value for the linear viscous elastic region [13.]

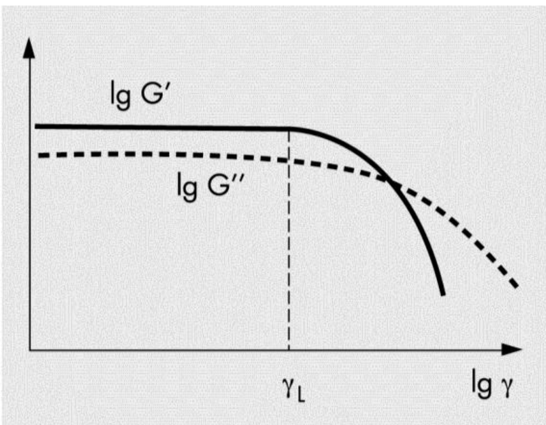


Figure 9. Oscillation: amplitude sweep [13].

For most paper coatings at small deformations below 1 % strain, the storage modulus is higher than the loss modulus. This means the coating colour is more solid like. With a higher deformation the situation is vice versa. The inter-particle association and flocculation of water soluble polymers and pigments create the viscoelastic properties of coating colours. [11, pp. 331]

5 Coating colours

Coating colour is an aqueous system which consists up to 90 per cent of pigment slurry which is the most important component of the coating colour. Coating colours are concentrated suspensions of solid particles, which can be either organic or mineral origin. Mineral particles consist of the pigments, such as talcum, calcium carbonate, titanium oxide, or clay. In a formulation there can be one or several different pigment types present at the same time. Organic particles are primarily latex and very seldom plastic pigments. Latex is a part of binder system, which is also a very important part of the formulation. In addition, coating colours include various additives. Water based liquid phase contains dissolved ions and organic matter. Basically these formulations are very simple, although the interactions between ingredients are very complex.
The basis of formulation is 100 parts of pigment; to which all additions are referred. Coating colour formulations (Table 1.) are individually designed for each product and coating method keeping the production costs in mind and in control. [1, pp. 13-14; 3, pp. 345; 14, pp. 45.]

Table 1. Examples of coating colour formulations [15, pp. 63-65].

Ingredient	**Low weight coated off set paper (LWC)**	**Precoating for wood free double coated fine paper.**
Clay	100	20
Calcium carbonate (CaCo3)	-	80
Styrene butadiene latex (SB)	10	10
Starch	-	-
Hardener	0.3	0.6
Stearate	0.5	-
Carboxyl methyl cellulose (CMC)	0.3	0.8

5.1 Pigments

Pigments are classified as main, special and additional pigments. The main pigments are the ones most commonly used in coating colours. Such pigments are ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), and kaolin clays. Various properties (Figure 10) of the pigments influence greatly on the coating colour rheology and properties of the coated paper. [3, pp.56]

Pigment	Chemical composition	Most particles (µm)	Particle shape	Density (kg dm^{-3})	Refractive index	ISO-Brightness
Kaolin clay	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	0.3–5	Hexagonal platy	2.58	1.56	80–90
GCC[a]	$CaCO_3$, $MgCO_3$ (2–3%)	0.7–2	Cubic, prismatic, platy	2.7	1.56–1.65	87–97
PCC[b]	$CaCO_3$	0.1–1.0	Variable, usually rodlike	2.7	1.59	96–99
Talcum	$MgO \cdot 4SiO_2 \cdot H_2O$	0.3–5	Platy	2.7	1.57	85–90
Gypsum	$CaSO_4 \cdot 2H_2O$	0.2–2	Roundish	2.3	1.52	92–94
Plastic pigment						
– solid	Polystrene most common	0.1–0.5	Spherical	1.05	1.59	93–94
– hollow		0.4–1.0	Spherical	0.6–0.9	1.59	93–94
Calcined kaolin	$Al_2O_3 \cdot 2SiO_2$	0.7 (median)	Aggregated plates	2.69	1.56	93
Titanium dioxide						
– anatase	TiO_2	0.2–0.5	Rodlike	3.9	2.55	98–99
– rutile	TiO_2	0.2–0.5	Roundish	4.2	2.70	97–98
ATH[c]	$Al(OH)_3$	0.2–2	Platy	2.42	1.57	98–100

Figure 10. Physical and optical properties of coating pigments [3, pp. 57].

Influence of a shape factor on the rheological properties of coating colours has been widely studied. The shape factor, aspect ratio, is determined by dividing the diameter of the particle with its thickness (Figure 11). The studies have shown some relationship between particle characteristics and rheological properties. Packing ability of particles is enhanced with a broad particle size distribution; this is associated with low viscosity. From another point of view, a smaller particle size decreases the distance between particles resulting higher viscosity at low shear rates. [16, pp. 3-5.]

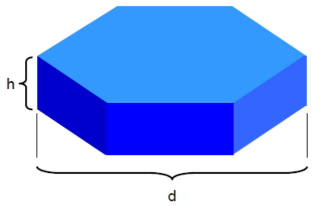


Figure 11. Aspect ratio of a pigment particle [15, pp.6].

Kaolin clay

Kaolin clay is one of the most commonly occurred mineral. From a chemical aspect kaolin is layered hydrous aluminosilicate. Main clay deposits are found in Cornwall England, United States, and Brazil. From coating and rheological point of view clay has good physical properties. Clay disperses well in water. Surface energy of clay is high, and therefore, it is highly hydrophilic. Viscosity of clay slurry is moderate, which allows higher solids content for coating colour. [15, pp. 16.]

Clay can be altered into calcinated form by heating it in 800 °C -1100 °C temperature. With calcinated clay the need of binder is bigger, because pigment particle has greater relative surface area. The rheology of calcinated clay is also different from traditional clay. Because of this, calcinated clay is dispersed in lower solids. Slurry is easily handled, but shows dilatancy if it is subjected to high shear rates. [3, pp. 57; 76, pp. 82-83; 15, pp. 16-17.]

Calcium carbonate

Natural calcium carbonate occurs as the mineral calcite in forms of chalk, limestone, and marble. GCC pigments are divided in broad and narrow particle size distribution products. Due to round particle shape (Figure 12.), the viscosity of $CaCO_3$ slurry is low even in high solid content. GCC has significantly lower relative surface area than clay. Therefore, replacing part of clay with GCC reduces the need of binder. [18, pp. 98; 15, pp. 20.]

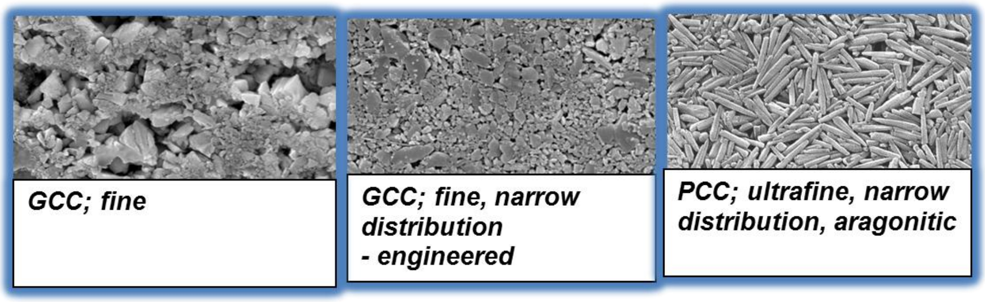


Figure 12. Different shapes of calcium carbonate [19].

Precipitated calcium carbonate (PCC) is a synthetic product made by direct carbonation of hydrated lime, known as the milk of lime process. It is more pure than GCC and finer.

Special and additional pigments

Talc is strongly hydrophobic platy mineral, which means it needs special attention when produced, and when it is used in water based coating colour. Talcum is dilatant and lamellar pigment [3, pp. 58]. Most European coating talc is obtained from the minerals from the transformation of silica aluminous rocks. Each rock has different ore composition, and therefore, each deposit has its own mineral composition. [20, pp. 110,113.]

Plastic pigments are organic pigments, which are used to partially replace the inorganic minerals to obtain better printability of paper. Plastic pigments are divided in two general classes, solid bead and hollow sphere [3, pp. 59]. There are very small differences on the rheological behavior of plastic pigment when compared to the main pigments. Although, it has been shown that the smaller particle sizes have slightly better blade runnability. [21, pp. 149.]

Alumina Trihydrate (ATH) known as aluminum hydroxide origins from bauxite. Bauxite for ATH is supplied by Australia, Guinea, and Greece as an example. To obtain ATH, bauxite ore has to be purified from other minerals and impurities. Soluble aluminium compounds are leached out in sodium hydroxide through the Bayer process. ATH slurry behaves like Newtonian liquid when produced correctly. Without proper dispersing agent and correct addition level, AHT produce thixotropic liquids or show pronounced dilatancy. [22, pp. 157,159.]

Titanium Dioxide (TiO_2) exists in three different crystal forms. Of these three, anatase and rutile are stable. TiO_2 pigments must be properly dispersed in the coating colour because undispersed agglomerates diminish the optical properties of TiO_2 [3, pp. 60]. TiO_2 pigment decreases the high shear viscosity of coating colours, because its small spherical particles settle between platy pigment particles, and thus keep the plates separate and thereby decrease the friction between the plates. [23, p. 173.]

5.2 Binders

Purpose of binders is to bind particles into each other and to the base paper. After pigments they are the second important substance in the coating colour. Also synthetic binders act as control aid for viscosity and water retention of coating colours. Most binders are synthetic by nature. Besides the synthetic, also natural binders are used in coating colours. Often multifunctional natural binders include starches and their derivatives, carboxyl methyl cellulose (CMC), and even soy protein, which is not discussed in this thesis, since it is more common in North American applications. Natural binders are water soluble and are delivered as dry product. They are primarily used as co-binders. [3, pp. 346.]

5.2.1 Lattices

Lattices are water insoluble petroleum based polymerization products. They are categorized into co-polymers of styrene and butadiene (SB), styrene and n-butyl acrylate (SA), and polyvinyl acetate (PVAc). Appearance of polymer based binders is white and milky like. Binders are often in 50 % solids dispersion in very fine particle size distribution. SB- latex is the most widely used binder, since it provides good rheology and paper properties. Properties given by lattices vary as illustrated in Table 2. [24, pp. 207.]

Table 2. Properties of various lattices [4, pp.189].

	SB-latex	PVAc-latex	Acrylate latex
Binding strength	++	-	+
Porosity	-	++	+
Light proofness	- -	+	++
Water proofness	+	-	+
Hardness	-	-	++
Anti blistering	-	++	+
Economics	+	++	- -

Monomers have different hardness and softness values; hence the amount of specific monomer in the polymer composition dictates the basic properties of latex. [24, pp. 207.]

5.2.2 Co-binders

Along synthetic binders co-binders have to be used to achieve acceptable runnability conditions. Water soluble co-binders are added in coating colour to modify viscosity and water retention of suspension. Apart from CMC, these binders need cooking before use. CMC is a versatile product, coming in low and high molecular weight products for different applications. At optimum level CMC adjusts water retention very efficiently, but at the same time it increases high shear viscosity, so finding the balance is at most importance. [3, pp. 111,113.]

Starch used in coatings originate e.g. potato and corn plants. The ratio of branched and non-branched polymer forms of starch depend on the foster plant as well as the shape and size of granules. Because of high viscous nature, raw starch has to be modified before use. [25, pp. 196.] Starch is a binding agent, although being water soluble, the binding strength is quite low. Starch does increase viscosity significantly and reduces water retention. [15, pp. 36-37.] *Polyvinyl alcoho*l (PVA) has superior binding power, but it cannot be used in large amount, since it would lead to serious rheological problems. [3, pp. 113.]

5.3 Additives

The final performance and quality of an end product is achieved with various additives. *Dispersing agent* is added to ensure that the pigment particles do not agglomerate [3, pp. 104]. *Optical brighteners* (OBA) increase the brightness value of the coated paper surface [3, pp. 123]. Use of *lubricants* reduces scratches in the coating and cracking on the super calender, thus preventing dusting. Stearate also improves the gloss of the paper. [3, pp. 119]. pH of the coating colour is adjusted usually with sodium or ammonium hydroxide [15, pp. 45].

5.4 Synthetic thickeners

The main purpose of thickeners is to adjust the viscosity and water retention of the coating colour to desired optimum level for ensuring the runnability of coating process and in order to achieve a good surface quality on the coated paper. The viscosity and water retention have several effects on the coating colour rheology and coated paper itself, as illustrated in picture 13. Thickeners have to interact with water molecules in order to increase the water retention. Interaction with other ingredients is also important. Especially interaction with pigment particles is necessary when adjusting the viscosity. [3, pp. 114]

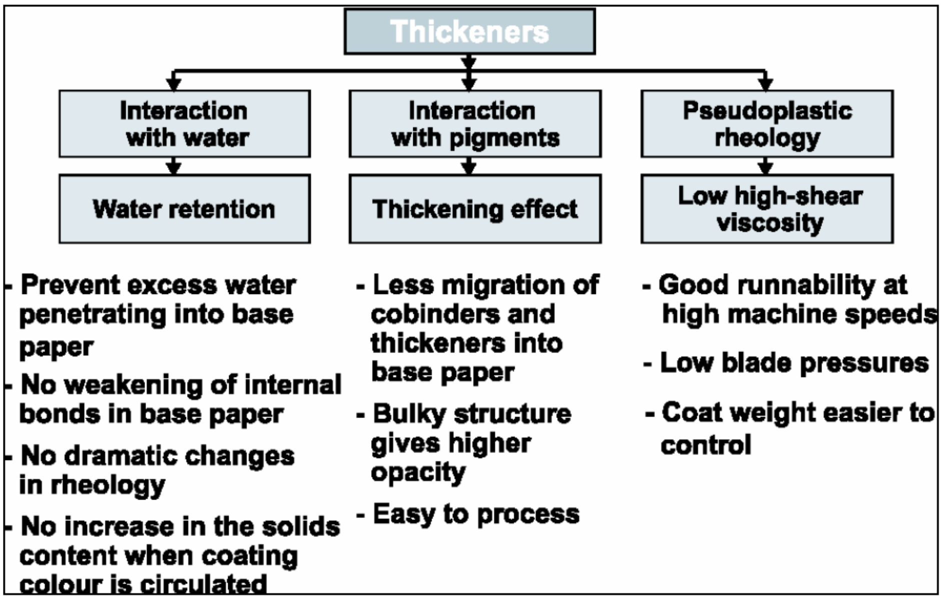


Figure 13. Main requirements of thickeners [3, pp. 115].

The main synthetic thickeners are PVA (discussed in paragraph 5), associative thickeners, and acrylic copolymers. [3, pp. 114].

5.4.1 Acrylic copolymers

Most of the acrylic copolymers are either copolymers of nonionic monomers and acrylic acid or methacrylic acid. These thickeners are also referred as alkali swellable emulsions (ASE). In order to dissolve in the aqueous phase and interact with pigments, the polymers need to be hydrophilic and polar. Acrylic thickeners have very low pH range. Figure 14 illustrates how adding alkali to the dispersion enables the carboxyl group dissociate and donate a proton, thus making the group anionic. [3, 26] In other words, the neutralization of alkali swellable emulsions leads to swelling of polymer particles and viscosity increase.

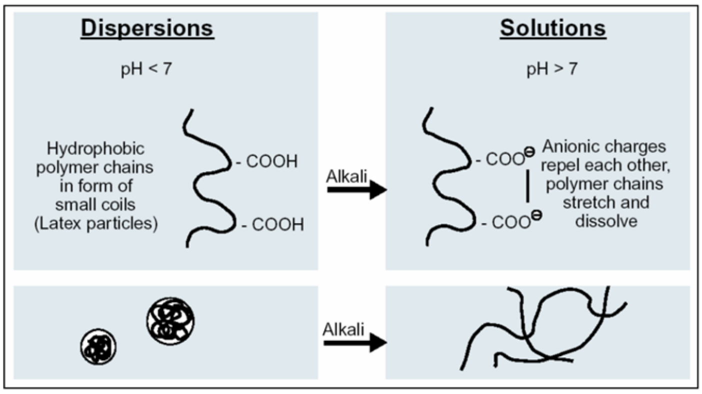


Figure 14. Dissolving principle of acrylic-based synthetic thickeners [26, pp. 257].

In Figure 14 can be seen, how anionic charges along the chain repel each other, thus forcing the chain stretch out and unfold. The present water molecules are attracted by the chain and attach to it. Thickeners bind a large quantity of water molecules along their polymer chain, thus increasing their volume and thereby occupying grater space in the dispersion. [26, pp.256-257]

Another important factor in thickening is the interaction with pigment particles. Acrylic thickeners have high affinity for pigments due to their polar functional groups which are attracted by the polar surfaces of the pigment. Figure 15 illustrates the difference in the thickening mechanism. [26. pp. 259].

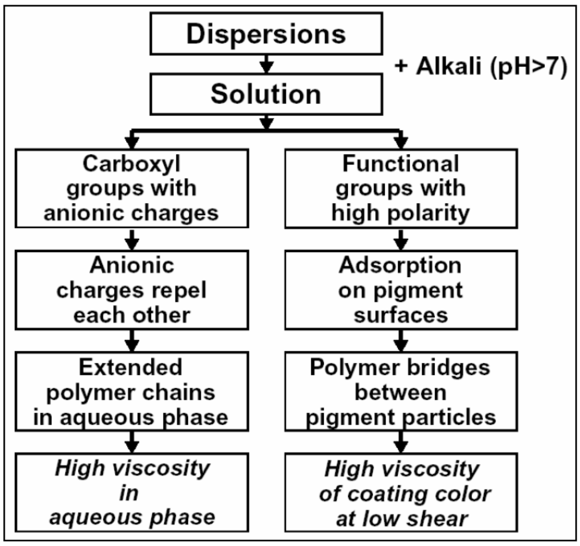


Figure 15. Thickening mechanism of the acrylic copolymers [26, pp.259].

The polymer chains adsorb on the surface of the pigment particles. The particles are then crosslinked by bridging mechanism. The increased viscosity is a result of cross-linking. [26, pp. 259].

5.4.2 Associative thickeners

While the associative thickener is hydrophilic and water soluble, the hydrophobic terminal groups of the polymer are completely insoluble in water. Their structure is similar to surfactants, therefore, they also tend to form micelles. Due to associative interaction between the hydrophobic side chains, the coating colour has a very high viscosity at low shear. Because of the weak van der Waals forces affecting the groups, the micelles break down under shear and the thickener molecules are oriented on the direction of the flow thus lowering the viscosity of the coating colour. Associative thickeners are divided into three groups according to the chemical structure, as shown in figure 16. [3. pp. 116-117]

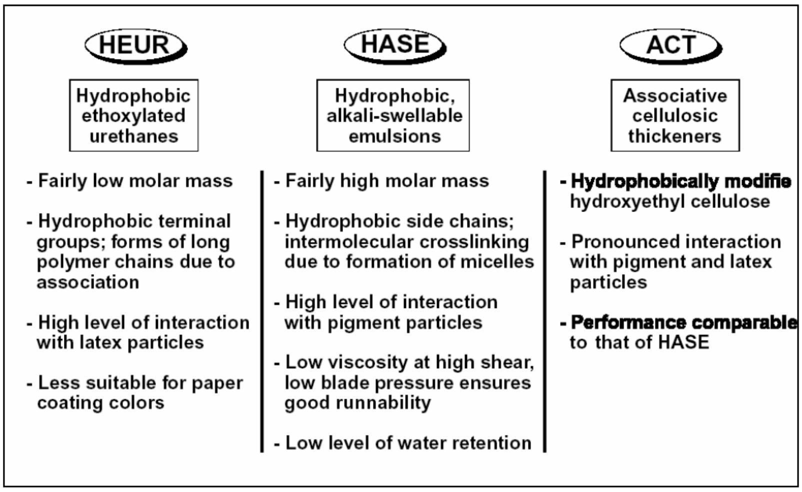


Figure 16. Types and properties of associative thickeners [26, pp. 265].

HEUR thickeners are short chained polymers with hydrophilic polyethylene glycol (PEG) backbone and hydrophobic groups attached at both ends. The increase in viscosity is based on the association of the hydrophobic terminal groups which makes them join together, and thus form longer chains. [26, pp. 265]

HASE thickeners are similar to ASE thickeners with the exception that in addition to acid groups, they also have long hydrophobic groups. The hydrophobic groups aggregate together in the water phase forming micelles, and therefore, HASE thickeners result enhanced viscosity. They also interact with other hydrophobic materials, especially lattices and surfactants [27].

ACT products consist of cellulose ethers with hydrophobic substituents. The most important product of this group is hydrophobic modified hydroxyethyl cellulose, which also has a high affinity to SB-latex and pigment particles.

6 Coating colour properties

Coating quality and coating process runnability are important factors from an economical and manufacturing point of view. Different properties of the coating colour formulation effect on the coating process itself, the most important properties being viscosity and water retention. Following properties are usually measured from the coating colour mixer and from the circulation as quality control.

6.1 Solids content

The solids content of the coating colour has an effect on the quality of the end product. In most cases, high-solids coating colour is preferred. High solids has a positive effect on gloss development, and it reduces the cost of drying energy. Too high or low solids content can affect directly to coat weight. Sudden increase in the solids may indicate poor water retention. Solids content is determined by using conventional owen drying or quick methods, which performance is based on either infrared or microwave drying. [1, p. 218; 3, p. 368; 5, p. 54].

6.2 Temperature

Usually coating colour temperature in the coating colour circulation lies between 40 and 50 Celsius degrees. Even small drop on temperature increases viscosity thus influencing flow of coating colour. Temperature is controlled online.

6.3 pH-value

pH-value depends on the coating application. Especially when synthetic thickeners are being used, the importance of the ph-value becomes very important.

6.4 Low shear viscosity

Low shear viscosity is usually measured with Brookfield viscometer. Brookfield measures relative viscosity, thus indicating only two things. Firstly, it is measured to observe the status of coating colour circulation. Secondly, low shear viscosity indicates, how low pressure is needed to pump the coating colour into the coating station.

6.5 High shear viscosity

High shear viscosity is an important factor when evaluating the rheological performance of the coating colour, since the shear rates can be as high as 10 million 1/s depending on the process. There are different viscometers for different share rates. With rotational viscometers, the maximum shear rate is relatively high and it is comparable to share rate of application phase, 10^4-10^5 1/s. The problem with this method is considerable shear heating and heat lowers the viscosity. When evaluating shear under blade, the capillary viscometer is the best choice. The capillary viscometer provides a wide range of shear with one measurement. In reality this is not often used, due to the considerably large volume of sample it needs. [12]

6.6 Water retention

Water retention (WR) is a result of pressure applied with an outside force. The mechanism is based on the coating colour's ability to bind water with functional groups. The principal of water penetration is shown in figure 17. [28, pp. 293]

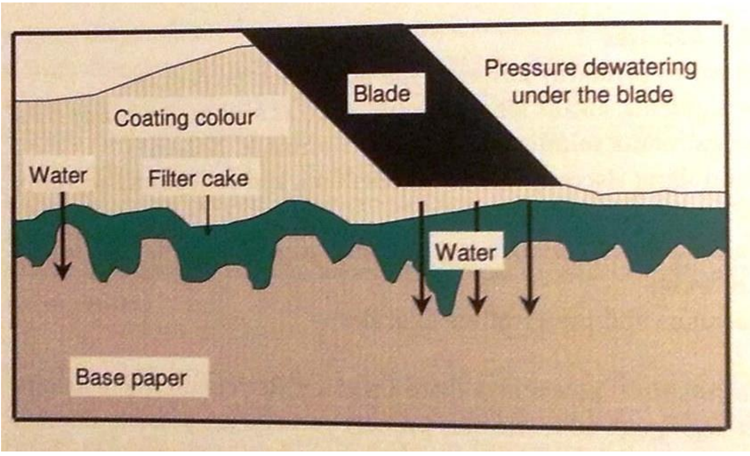


Figure 17. Influence of water retention on coating colour application [3, pp. 348].

Water starts to move immediately after the coating colour and base paper have come to contact. Water continues moving until the immobilised coating structure is formed. [28, 293] Water retention can be measured either dynamically or statically the latter being more common method. Too low or high WR have both negative influences on a process. For example, a rapid increase of solids content is a result of too low water retention. This makes coat weight control more difficult. Low water retention also enables binder migration in the water phase. [29]

7 Key measurements

7.1 ÅA-GWR

ÅA GWR (Åbo Akademi Gravimetric Water Retention) is a static water retention analyser. Static water retention measurement indicates the quantity of the aqueous phase leaving from the coating colour and penetrating into the base paper. The unit of the water retention is indicated as g/m^2. The measurement is based on membrane filtration under applied pressure. [5, p. 368]. With this method there lies a possibility, that minor pigment particles are able to migrate through the membrane, thus, making the interpretation of results more challenging [5, p.54.]

Figure 18. ÅA-GWR measuring device.

Procedure

Water retention is measured through 5 µm polycarbonate membrane and blotting paper as a base paper. The measuring cylinder is filled with 10 mill litres of coating colour. Chamber is closed with a cap. Pressure of 0.3 bar is applied after 15 seconds delay. Chosen measuring time is 120 seconds, and after this time pressure stops automatically. The system is let to rest for 15 seconds before removing the cylinder. The base paper is weighed. Water retention is calculated with the equation,

$$(B - A) * 1500$$

where A is the weight of the base board before analysis, and B is the weight of the base board after the analysis.

7.2 Hercules Hi-Shear Viscometer

High shear viscosity is measured with Hercules DV-10 rotational viscometer. It utilizes concentric cylinders (Figure 19) with a well-defined geometry to measure a fluid's resistance to flow. The gap between inner bob and outer cylinder is very small. When a coating colour sample is confined between the bob and cup, rotation on the bob generates a velocity gradient across the gap. This gradient is termed shear rate and defined as the change in linear viscosity (cm/sec) between two fluid elements divided by their distance in centimetres. Thus, the shear rates are expressed in reciprocal seconds (sec-1). Absolute or apparent viscosity for non-Newtonian fluids can be calculated at any shear rate and up to a selected maximum speed of rotation. [30, pp. 2].

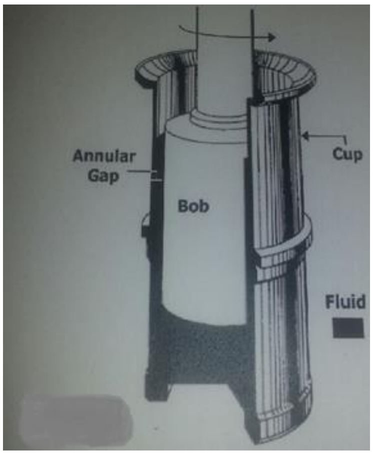


Figure 19. Hercules measuring system.

Procedure

Coating colour is measured using "A" bob. Sample information and density are filled in the measuring template. The measuring cylinder is filled to the mark, approximately 20 mill liters. After running the sample viscosity values can be found in the calculating sheet.

8 Experimental part

The study was carried out by testing six synthetic thickeners (labelled from A to E) in two different kinds of formulations. The idea of the two different pigment systems was to study also, how pigment particle size, and shape factor influence on the thickening effect. GCC has an aspect ratio of 1 and clay used in the study has aspect ratio between 15 and 30. The first formulation (table 3 and 4) had GCC1/GCC2 ratio of 30/70. Reference formulation had 13 parts of SB- latex. Total binder amount of the experimental formulations was 9 parts of latex. Thickeners were tested on three dosage levels. Target SC for the formulations was maximum solids and the target pH was set to pH 9. Reference coating colour was made also without pH adjustment in order to see the effect of the pH adjustment.

Table 3. Coating colour formulations for GCC1/ GCC2.

	Ref CC1	CC2	CC2	CC3	CC4	CC5	CC6	CC7	CC8	CC9	CC10
GCC1	30	30	30	30	30	30	30	30	30	30	30
GCC2	70	70	70	70	70	70	70	70	70	70	70
SB	13	13	5	5	5	5	5	5	5	5	5
SA	-	-	4	4	4	4	4	4	4	4	4
HASE A	0,1	0,1	0,05	0,1	0,2	-	-	-	-	-	-
HASE B	-	-	-	-	-	0,05	0,1	0,2	-	-	-
HASE C	-	-	-	-	-	-	-	-	0,05	0,1	0,2
HASE D	-	-	-	-	-	-	-	-	-	-	-
ASE E	-	-	-	-	-	-	-	-	-	-	-
Modifier	-	-	-	-	-	-	-	-	-	-	-
pH target	-	9	9	9	9	9	9	9	9	9	9
SC target	max	max	max	max	max	max	max	max	max	max	max

Table 4. Coating colour formulations for GCC1/GCC2 (continued).

	CC11	CC12	CC13	CC14	CC15	CC16	CC17	CC18	CC19
GCC1	30	30	30	30	30	30	30	30	30
GCC2	70	70	70	70	70	70	70	70	70
SB	5	5	5	5	5	5	5	5	5
SA	4	4	4	4	4	4	4	4	4
HASE A	-	-	-	-	-	-	-	-	-
HASE B	-	-	-	-	-	-	-	-	-
HASE C	-	-	-	-	-	-	-	-	-
HASE D	0,1	0,2	0,3	-	-	-	-	-	-
ASE E				0,1	0,2	0,3	-	-	-
Modifier				-	-	-	0,1	0,2	0,3
pH target	9	9	9	9	9	9	9	9	9
SC target	max	max	max	max	max	max	max	max	max

The second formulation (table 5) had 70/30 ratio of GCC and clay. Binder system of the coating colour consisted of 8 parts of co-binder starch and 4, 5 parts of SA- latex. The second formulation was tested with only with one thickener dosage level. Target solid content was set to 62, 5 w/% and the target pH was set to pH 9.

Table 5. Coating colour formulations for GCC/Clay formulations

	REF	CC2	CC3	CC4	CC5	CC6	CC7
GCC	70	70	70	70	70	70	70
Clay	30	30	30	30	30	30	30
Dispersing agent	0,15	0,15	0,15	0,15	0,15	0,15	0,15
Strach	8	8	8	8	8	8	8
SB latex	9	-	-	-	-	-	-
SA latex	-	4,5	4,5	4,5	4,5	4,5	4,5
Hardener	2,5	2,5	2,5	2,5	2,5	2,5	2,5
OBA	0,5	0,5	0,5	0,5	0,5	0,5	0,5
HASE_A	0,15	0,15					
HASE_B			0,15				
HASE_C				0,15			
HASE_D					0,15		
ASE_E						0,15	
Modifier_F							0,15
SC target	62,5	62,5	62,5	62,5	62,5	62,5	62,5
pH target	9	9	9	9	9	9	9

The coating colours were prepared under constant stirring in order to mix the dispersion thoroughly. The components are presented in appendix 1 in adding order. pH level of the formulations was adjusted to 9 before adding the synthetic thickener in order to supply enough alkali in to the dispersion. Final solids content and pH level were adjusted at the end of the coating colour preparation.

Standard measurements were carried out. Water retention was measured according to the ÅA-GWR instructions. Brookfield 100 rpm and 50 rpm were measured with Brookfield DV I+ device, according to standard SCAN-P 50:84. High shear measurements were carried out using Hercules DV 10 rotational rheometer. Also pH, solids content, temperature and density of the coating colours were measured.

9 Results

9.1 GCC based formulation

9.1.1 Effect of pH adjustment on the rheology of the reference sample.

Effect of the pH adjustment was seen in all rheology measurements. Measured relative viscosity was doubled without pH adjustment. Likewise high shear viscosity and water retention value were higher when pH was not adjusted. This is due to the lack of alkali in the thickener containing dispersion, which made the coating colour unstable. [26, pp. 257.] Also the calcium carbonate is soluble as a function of pH, and therefore soluble calcium ion can take part in agglomeration. The thickener simply did not perform properly, because alkali was not added to the dispersion..

9.1.2 Effect on water retention and Brookfield viscosity

The water retention vs. Brookfield viscosity are presented in figure 20. SA/SB latex combination had a stronger thickening tendency that that of reference sample. This is due to the fact that the novel SA latex has smaller particle size. With 0.1 part addition, samples A, B, and E were roughly in the same viscosity range. Effect on viscosity was moderate with HASE D. Sample C had the strongest effect on viscosity, especially, when addition of the thickener was increased. Modifier seemed to have very moderate thickening effect, since it had much shorter chain length than synthetic thickeners.

Sample E (ASE) reached the best water retention value, and it showed positive influence on the water retention with lower addition levels, which is good from an economical aspect. The other thickeners, apart from D and modifier, reached the same WR range, but ASE seemed to be more effective on lower addition levels.

Difference between thickening effect of HASE type modifiers might be in the molecular mass and the maximum degree of branching or internal crosslinking . Higher molecular weight modifiers have longer chains, and therefore also more COO^- groups, which can attract OH-groups. This way they thicken the water phase more effectively. Most of the modifiers are acrylic base, and they have a high affinity for pigments. [26, pp. 257.]

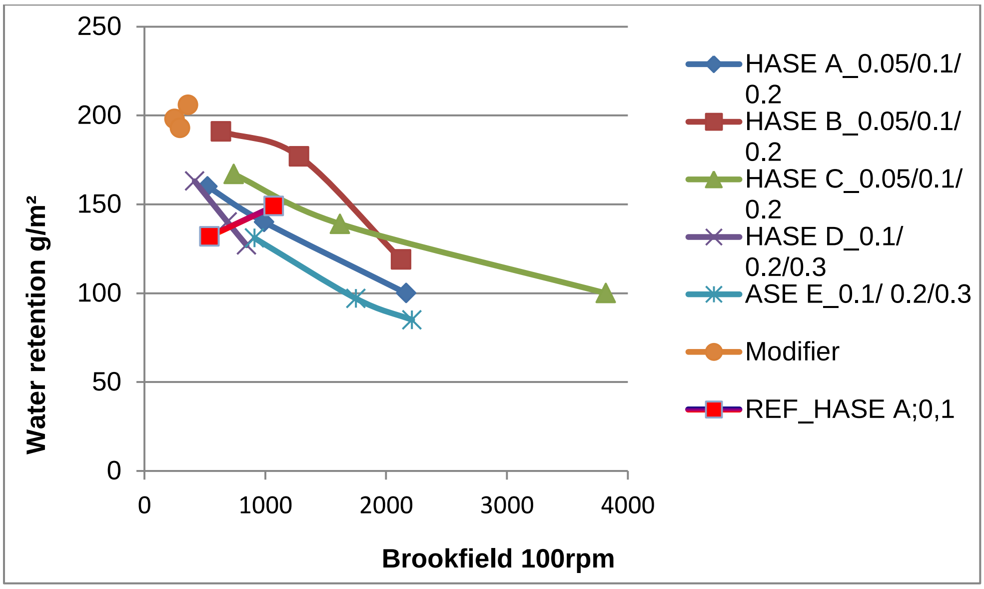


Figure 20. Water retention vs. relative viscosity.

9.1.3 Effect on high shear viscosity and it's relation with water retention

Reference sample had significantly lower high shear value than the SB/SA latex formulations. The chemical interaction of SB latex/thickener is not as strong as that of SA/SB combination. Figure 21 illustrates how the dewatering rate decreased as a function of increasing high shear rate. Increase of modifier thickened the water phase more effectively.

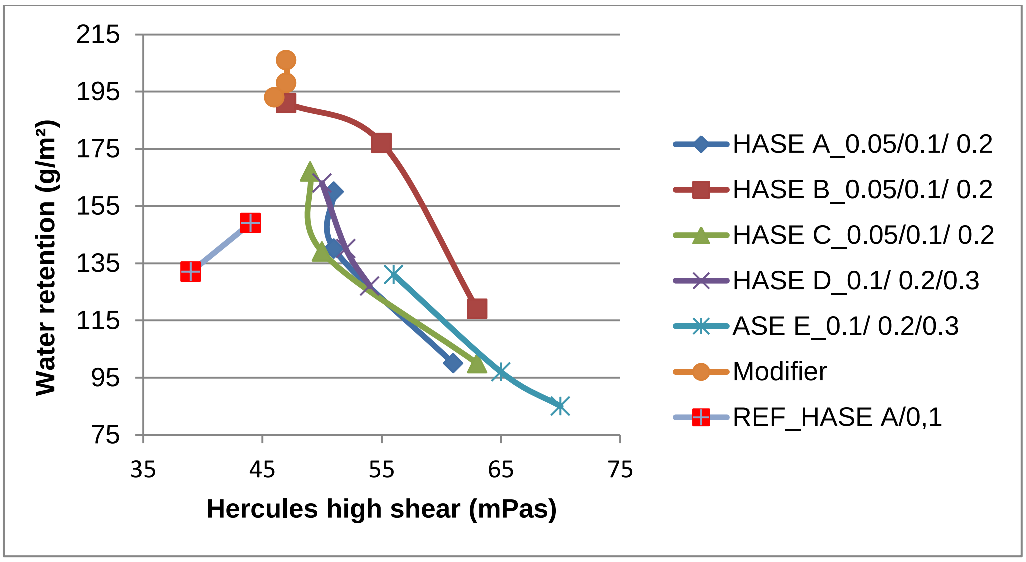


Figure 21. Relation of water retention and high shear viscosity.

HASE thickeners had increase in low shear values (figure 22] .This increase was not seen in the same extent in the high shear values, because of the breakdown of the micelles under high shear. The modifier did not have effect on high shear.

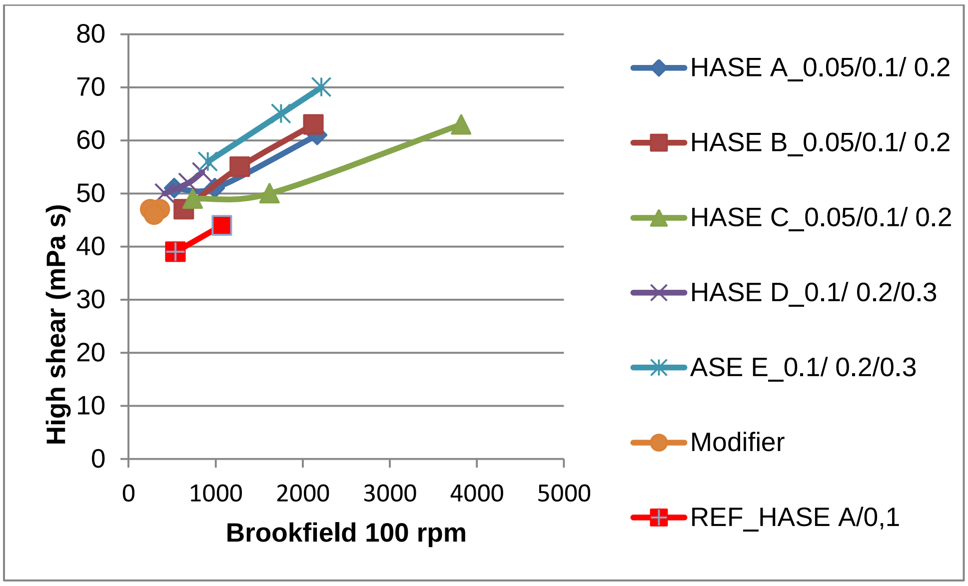


Figure 22. Relation between high shear and low shear values

9.2 GCC/Clay formulation

The clay used in the study has very low levels of fine particles, as low as below 0,2 um. The shape of the clay is somewhat blocky. The aspect ratio of the clay is between 15:1 and 30:1. GCC formulations had more variation on low shear viscosities. GCC used in this study has broad particle size deviation, which decreases viscosity because of the better packing ability. Figure 23 illustrates viscosities of the GCC/clay formulation.

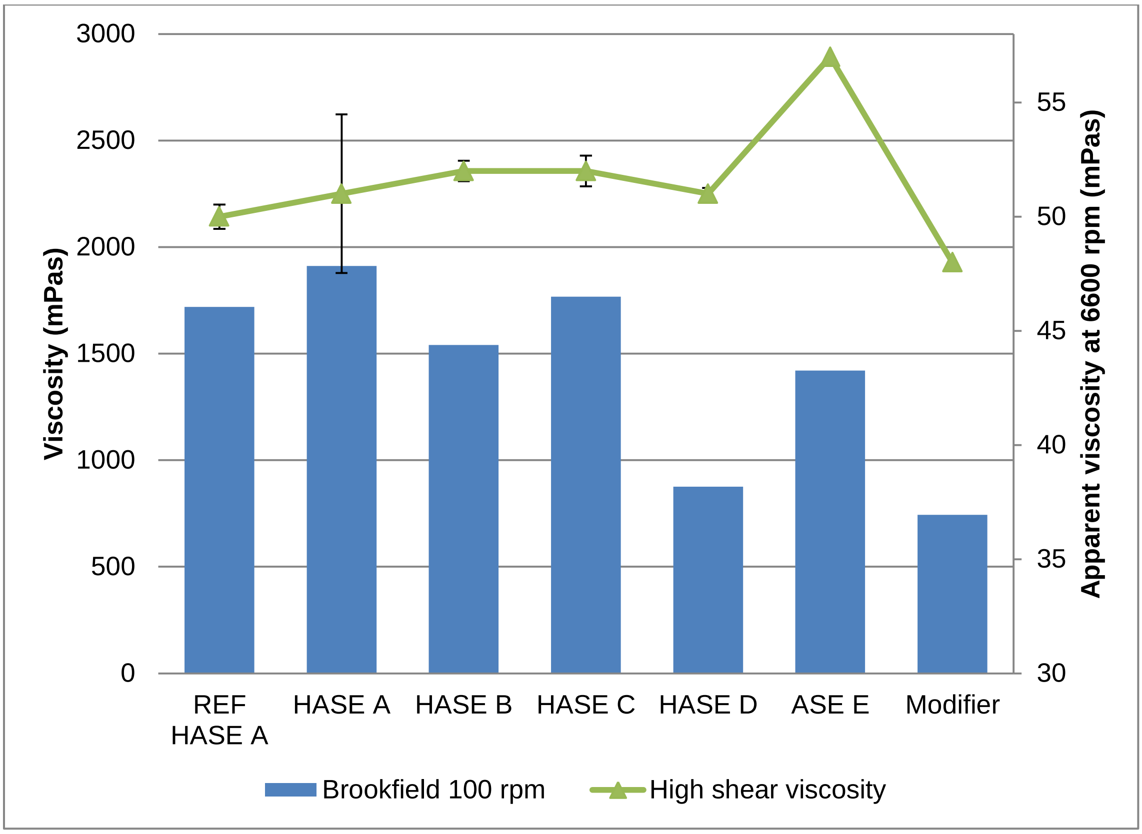


Figure 23. Relative viscosity vs. apparent viscosity of GCC/clay formulations with 0.15 addition of thickener.

Another reason for the different behavior between formulations is that, the ionic strength on the association of HASE polymers has effect on the rheology. The pigment combination was different with the two formulations, and furthermore, the GCC/clay formulation had more components in the recipe. The chemical nature of the GCC/clay formulation was totally different [32]. *Samya el- Sherbiny* and *Xiao Huining* showed in their study [33] that the absorption level of the thickener on the pigment particle is strongly affected by the surface structure of the pigment. Thickeners show greater affinity towards clay pigment than GCC.

9.2.1 Effect on water retention

The overall level of water retention of the coating colours was much lower than that of GCC formulations. It is more likely due to the starch in the formulation, than the presence of the clay. Though, the low aspect ratio of the clay pigment can decrease water retention. In the Figure 24 can be seen that the reference formulation had the lowest dewatering rate. Between HASE and ASE type thickeners can be seen how ASE thickener had greater influence on water retention. HASE D had as low influence to the viscosity as the modifier.

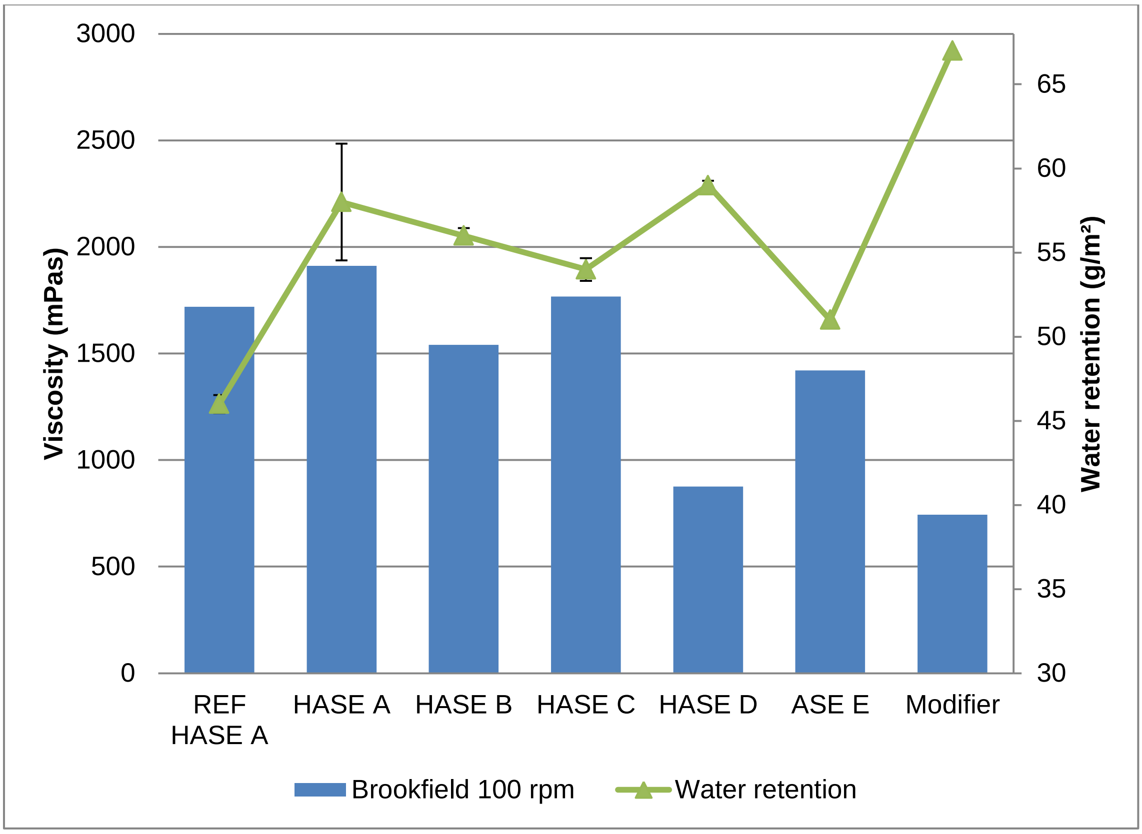


Figure 24. Relative viscosity (Brookfield100) vs. water retention.

10 Conclusions

The study has showed that the amount and type of the modifier greatly influence to the properties of the coating colour. Also the chosen pigment system has pronounced effect on the viscosity build up. The surface structure of the pigment has significant role when the effect of thickener is under inspection. There is a big difference between even between the same type of thickeners. Generally, HASE type of thickeners have a high influence on low shear viscosity build up and low high shear effect. This type of thickeners have a moderate effect on water retention.

ASE thickeners have a moderate influence on low shear viscosity and low to high high shear profile. It is more effective as water retention aid than the HASE type of thickener. Overall, the study has showed clear correlation between rheology measurements. Increase in high shear profile decreases the water retention value. Increase in high shear has less effect on clay-based formulation than plain GCC. The role of modifier was left a little unknown, since it had very little or non-effect on rheology of the coating colours. The influence of modifiers on the coating colours is a very complex matter, and it has been studied widely. There are numerous variables which together influence the thickening effect. In this thesis the effect of the modifiers on the elongational properties of the coating colour were not under inspection, and that would be interesting to study in the future.

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Correlation between variables

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GCC formulation

	Thickener	*Brookfield 100*	*Brookfield 50*	*pH*	*SC*	*Density*	*Water retention*	*HerculesHigh Shear*
Thickener	1							
Brookfield 100	0,326043	1						
Brookfield 50	0,316393	0,998572	1					
pH	0,150099	0,145055	0,133903	1				
SC	0,155475	0,197605	0,193117	-0,04645	1			
Density	-0,42192	-0,59116	-0,58012	0,129826	-0,16282	1		
Water retention	-0,39549	-0,74086	-0,72312	-0,09696	-0,10047	0,642525	1	
HerculesHigh Shear	0,486428	0,759971	0,739997	0,328897	0,112621	-0,45938	-0,73357	1

GCC/clay formulation

	BR100	*BR50*	*density*	*pH*	*SC*	*WR*	*HerculesHigh Shear*
BR100	1						
BR50	0,994924	1					
density	0,165277	0,171229	1				
pH	0,881694	0,893518	0,065949	1			
SC	0,29149	0,283053	0,186921	0,414781	1		
WR	-0,65743	-0,62728	0,059418	-0,60911	-0,78459	1	
Hercules	0,290963	0,222849	0,132446	0,290978	0,567962	-0,49652	1